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Published in:

Physica C: Superconductivity and its Applications

DOI:

[10.1016/S0921-4534\(98\)00417-1](https://doi.org/10.1016/S0921-4534(98)00417-1)

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

1998

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Els, G., Lemmens, P., van Loosdrecht, P. H. M., Guntherodt, G., Lang, H. P., Thommen-Geiser, V., & Guntherodt, H. J. (1998). Determination of the superconducting energy gap of Rb₃C₆₀ by electronic Raman scattering. *Physica C: Superconductivity and its Applications*, 307(1-2), 79 - 86.
[https://doi.org/10.1016/S0921-4534\(98\)00417-1](https://doi.org/10.1016/S0921-4534(98)00417-1)

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Determination of the superconducting energy gap of Rb_3C_{60} by electronic Raman scattering

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Received 30 January 1998; revised 3 August 1998; accepted 17 August 1998

Abstract

Rb_3C_{60} single crystals ($T_c = 31 \pm 0.5$ K) have been investigated by Raman spectroscopy as a function of temperature with respect to phonon and electronic scattering. One of the intermolecular $\text{Rb} - \text{C}_{60}$ phonons observed showed changes upon cooling below the superconducting transition temperature indicating a strong coupling to the electronic system. Special attention was given to the electronic Raman scattering cross section of Rb_3C_{60} . A clear reduction of the scattering intensity for low frequencies has been observed below T_c . This reduction is identified as the opening of the superconducting energy gap for which we find $2\Delta/k_B T_c = 4.0 \pm 0.5$. This value was observed for several different scattering symmetries, in agreement with the proposed s-wave superconducting order parameter. © 1998 Elsevier Science B.V. All rights reserved.

PACS: 74.70.Wz; 74.25.Gz; 78.30.-j

Keywords: Superconductivity; Fullerides; Raman scattering; Energy gap

1. Introduction

The discovery of superconductivity in alkali-metal-doped C_{60} at relatively high transition temperatures [1,2] was another big surprise after the discovery of high- T_c cuprate superconductors. In the related graphite intercalation compounds, such as RbC_8 ($T_c = 0.15$ K), the superconducting transition temperature is a factor of 10–200 lower. The initial discovery of superconductivity in K_3C_{60} sparked an intense research effort in order to understand the

mechanism and superconducting properties of alkali metal doped fullerides [3].

The dependence of the transition temperature on the lattice constant gave strong indication that the superconductivity is induced by electron–phonon coupling, i.e., the weak coupling BCS formalism should be applicable [4,5].

The half occupied LUMO (lowest unoccupied molecular orbital) in the A_3C_{60} ($A = \text{K}, \text{Rb}$) compounds has t_{1u} symmetry. Group theory predicts that these states couple to the A_g and H_g intramolecular phonon modes [6–8]. Since these are just the phonon modes that are allowed in Raman scattering, this technique should be highly suited to provide valu-

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able information about the electron–phonon coupling.

The phonons are spread over a wide frequency range starting from roughly 20 cm^{-1} for the intermolecular modes up to 1600 cm^{-1} for the intramolecular phonon modes. This lead to a discussion which of the intermolecular [9–13], the high [7] or the low frequency [14,15] or all [16] intramolecular modes couple predominantly to the electrons and are therefore responsible for the superconductivity of the A_3C_{60} compounds. Values reported for the electron–phonon interaction λ are in the range 0.2–2.1 [7,14–20], with the general tendency that the low λ -values will involve the high frequency phonons and the high λ -values require the low frequency phonons to couple predominantly to the electrons.

To confirm the ideas of phonon mediated superconductivity it is also important to determine the reduced gap value $2\Delta/k_B T_c$, which in the weak coupling limit should be 3.52. The early works gave values for the gap which did not answer the question whether the A_3C_{60} compounds are strong or weak coupling superconductors, see for instance Refs. [21,22]. These works seemed to be strongly influenced by a poor quality of the available samples at that time. Recent investigations on high quality samples gave values for $2\Delta/k_B T_c$ between 3.45 and 4.2 [23–26].

Using electronic Raman scattering one may determine the superconducting gap by the observation of changes of the electronic scattering intensity upon cooling below T_c . Generally, electronic Raman scattering arises due to mass fluctuations of electrons near the Fermi surface, yielding a broad scattering continuum in the spectra. As a consequence of the redistribution of the density of states in the superconducting state, one expects a decrease of the electronic scattering intensity for frequencies below 2Δ . In addition, polarization dependent measurements may provide information about the symmetry properties of the order parameter [27]. Although electronic Raman spectroscopy was successful in determining the superconducting gap and the symmetry of the order parameter in high-temperature superconductors (HTSC) [28], no clear results have been obtained so far for the A_3C_{60} compounds. Preliminary Raman investigations on low quality powder samples ($T_c = 28\text{ K}$) yielded a reduced gap value of $2\Delta/k_B T_c = 7.7$

± 1.1 [29]. With the availability of high quality single crystals with strongly improved superconducting properties it is worthwhile to make a more thorough investigation of the superconducting properties on Rb_3C_{60} using inelastic light scattering. We therefore decided to perform temperature and polarization dependent Raman scattering experiments on Rb_3C_{60} single crystals in order to obtain more definitive insight into the coupling mechanism as well as towards the magnitude and symmetry of the superconducting order parameter.

2. Experimental

The Rb_3C_{60} single crystals used in this work were obtained by annealing high purity sublimation grown C_{60} single crystals ($6 \times 2 \times 2\text{ mm}^3$) with a stoichiometric amount of rubidium. The doping level was checked by Raman measurements of the position of the $A_g(2)$ mode. The Rb_3C_{60} samples had $T_c = 31 \pm 0.5\text{ K}$, measured by dc susceptibility using SQUID magnetometry. The transition width, defined as the temperature difference between $0.1\chi_m$ and $0.9\chi_m$, where χ_m is the magnetic susceptibility, was found to be relatively sharp ($\approx 3\text{ K}$). The superconducting Meissner phase for $H = 2\text{ G}$ was about 8–12% calculated from the ratio $\chi_m(\text{field cooled})/\chi_m(\text{zero field cooled})$.

For the Raman measurements we used the 514.5 nm excitation line of an Ar^+ -laser in a quasi-back-scattering geometry. The incident power was kept below 4 W/cm^2 to avoid any photoinduced effects or additional heating in the laser focus. To prevent degradation of the Rb_3C_{60} single crystals great care was taken to avoid any contact with air or oxygen throughout the preparation and the experimental procedures. A special sample holder was constructed to mount the sample under oxygen-free conditions into the cryostat. The samples were cooled in He contact gas in the temperature range of 4.2–300 K. The scattered light was analyzed using a Dilor XY spectrometer with a liquid nitrogen cooled CCD detector.

3. Results and discussion

The symmetry of the free C_{60} molecule is I_h . The Raman selection rules give $A_g + H_g$ symmetry components for parallel and H_g for crossed polarization

of incident and scattered light. As usual we will indicate in the following the intramolecular modes according to the I_h point group. Rb_3C_{60} single crystals have the structure $\text{Fm}\bar{3}\text{m}$ (O_h^5) [30]. The crystals used in this study showed faces with interplanar angles of roughly 90° and 110° which are identified as the {100} and {111} faces, respectively [31]. Polarized Raman scattering experiments on the different natural crystal faces allow one to partially separate the excitations according to their crystal symmetry. Measurements on the {100} face give the $A_g + E_g$ symmetry components for parallel polarization and $T_{1g} + T_{2g}$ for crossed polarization. On the {111} face the parallel polarization gives $A_g + E_g + T_{2g}$ and crossed polarization $E_g + T_{1g}$ symmetry components. The electronic properties should in principle exhibit the full crystal symmetry. Consequently, we will denote the intermolecular phonon modes and the electronic scattering contribution according to the crystal symmetry.

Fig. 1 shows polarized Raman spectra recorded at 4.2 K and 35 K for three different scattering geometries [Fig. 1 upper parts, (a) $A_g + E_g$, (b) $E_g + T_{1g}$,

(c) $T_{1g} + T_{2g}$]. The 35 K spectra were shifted upwards for clarity. Note the logarithmic intensity scale in the upper part of Fig. 1a. The spectra show the $A_g(1)$ at 496 cm^{-1} and the two H_g intramolecular phonon modes at 263 and 410 cm^{-1} . Additional peaks are observed at 478 , 520 and 546 cm^{-1} . They can be attributed to gerade modes of the molecule activated through the crystal field [32].

Fig. 2 shows the $A_g + E_g$ spectra from Fig. 1a in the frequency range from 10 to 200 cm^{-1} . A spectrum observed at 10 K is shown additionally. Two weak peaks are observed in the 4.2 K spectrum, centered at roughly 41 and 84 cm^{-1} , respectively. The modes are also clearly observed in $E_g + T_{1g}$ scattering geometry (Fig. 1b), whereas in the $T_{1g} + T_{2g}$ geometry, though also observable, they are less pronounced (Fig. 1c).

The peak at 84 cm^{-1} with a full width at half maximum (FWHM) of 9 cm^{-1} shows a significant broadening and softening by raising the temperature above T_c . At 35 K the mode remains observable as a broad structure. The FWHM was estimated to be roughly 20 – 30 cm^{-1} . The center of the phonon has

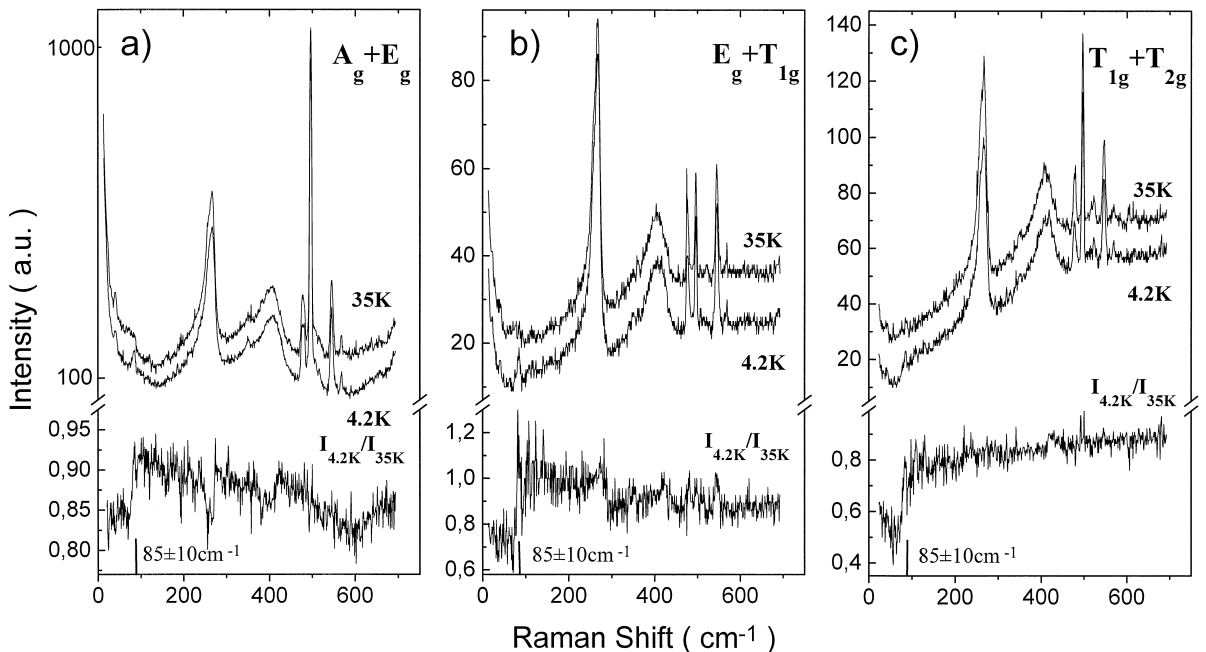


Fig. 1. Raman spectra of a single crystal of Rb_3C_{60} for the scattering symmetries $A_g + E_g$ (a), $E_g + T_{1g}$ (b) and $T_{1g} + T_{2g}$ (c). The upper parts show the original spectra obtained at 4.2 K and 35 K . The 35 K spectrum has been given an offset for clarity. Please note the logarithmic intensity scale in (a). The lower part shows the normalized spectra ($I_{4.2\text{K}}/I_{35\text{K}}$). The gap position is indicated.

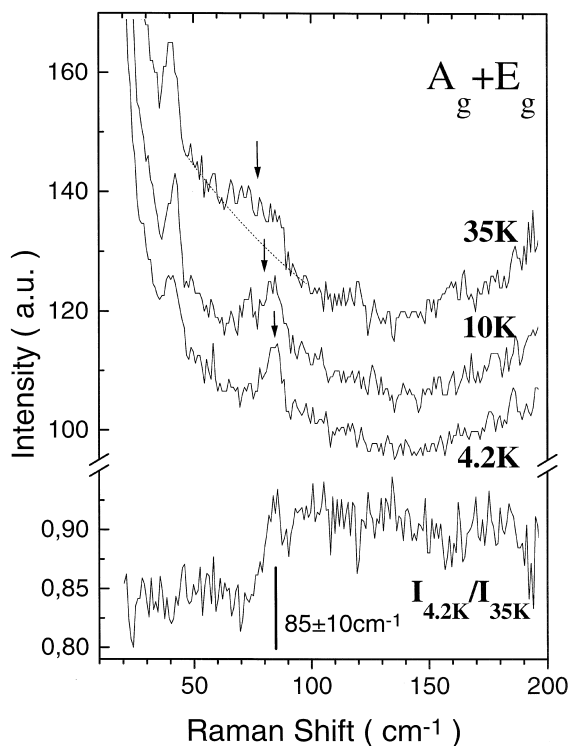


Fig. 2. Raman spectra of Fig. 1a ($A_g + E_g$) on an expanded scale from 10 to 200 cm^{-1} . The original spectra at 4.2 K and 35 K are shown in the upper part. A spectrum observed at 10 K is shown in addition. The 10-K and 35 K spectra have been given an offset for clarity. The dashed line is a guide to the eye indicating the shape of the scattering background. The estimated peak positions of the T_{2g} phonons are indicated. The lower part shows the normalized spectrum ($I_{4.2\text{K}} / I_{35\text{K}}$).

shifted to lower frequencies and was estimated to be at 78 cm^{-1} . The 41 cm^{-1} mode shows no obvious dependence on the temperature.

These low frequency modes are assigned to the intermolecular vibrational and librational modes of the crystal. Group theory yields a T_{2g} Raman active intermolecular vibration and a T_{1g} libration mode for the disordered $\text{Fm}\bar{3}\text{m}$ space group. Because libration modes are expected to have lower energies than the intermolecular vibration modes we can assign the 41 cm^{-1} excitation to the T_{1g} libration and the 78 cm^{-1} ($T = 35 \text{ K}$) excitation to the T_{2g} intermolecular vibration mode. The position and width of this vibration mode at 35 K is comparable to a reported mode observed at 300 K which was attributed to a disorder

induced density of states (DOS) of the T_{2g} Rb-C_{60} vibration [33]. The observed spectra for different scattering geometries (Fig. 1) imply that the Rb-C_{60} phonon at 78 cm^{-1} ($T = 35 \text{ K}$) should not have pure T_{2g} symmetry and may also be influenced by disorder. Two other modes at 30 and 41 cm^{-1} were observed in a Raman scattering study on C_{60} single crystals [34]. They were suggested to belong to C_{60} libration modes. Besides the 30 cm^{-1} mode which could not unambiguously be observed by us, our measurements are in agreement with previous results [33,34].

The changes in width and position of phonons due to a superconductivity-induced self-energy renormalization were investigated in Ref. [39] for high- T_c superconductors. It was shown that phonons with frequencies $\omega/2\Delta < 1.1$, which seems to be the appropriate assumption in our case, should show a softening of the peak position and a decrease of the width below T_c , which can be explained by the reduced electronic DOS in this frequency and temperature region. The reduction of linewidth observed in our Rb_3C_{60} spectra seems therefore to be consistent with this theory. However, the observed phonon DOS for $T > T_c$ imply that the observed effects might not be explained properly by such a model.

The reduction of the width and also the shift to higher frequency of the 78 cm^{-1} Rb-C_{60} vibration upon reducing the temperature below T_c clearly shows that these effects are superconducting induced. This supports the idea that the low frequency intermolecular modes play an important role for the electron-phonon coupling in A_3C_{60} . In general it is believed that intermolecular modes play only a minor role for the superconductivity in fullerenes because isotope effect measurements showed no significant change of the transition temperature upon doping with different alkali isotopes [35–37]. However, as was pointed out in Ref. [37], although the contribution of the alkali modes to T_c is at best small, the contribution of a low-frequency alkali mode to the electron-phonon coupling can be substantial. The role of intermolecular phonon modes for superconductivity was also confirmed by other authors [10,11]. Experimental hints for the importance of low frequency intermolecular modes came from resistivity and inelastic neutron scattering (INS) experiments [13,38]. Especially the INS data showed a weak

anomalous temperature dependence of low energy phonons in K_3C_{60} at T_c . Our Raman data show also directly the relationship between the intermolecular modes and superconductivity.

A comparison between spectra with different scattering symmetry shows a difference in the shape of the electronic scattering continuum (Fig. 1, upper parts). For $A_g + E_g$ (Fig. 1a) the continuum appears to be nearly constant in the region from 700 cm^{-1} down to 150 cm^{-1} . Below 150 cm^{-1} the Rayleigh scattered light leads to an enhancement of the intensity. For $E_g + T_{1g}$ (Fig. 1b) and more pronounced for $T_{1g} + T_{2g}$ (Fig. 1c) the electronic scattering continuum is constant between 700 and roughly 450 cm^{-1} and decreases linearly to lower frequencies.

A comparison of the intensity of the spectra in Fig. 1a and b clearly shows that the electronic scattering in the $A_g + E_g$ spectrum is dominated by the A_g component. The A_g component is by a factor 8 to 10 larger than the other symmetry components. The A_g contribution in electronic Raman scattering is normally assumed to be weak due to the screening of isotropic charge fluctuations by long range Coulomb interactions. A similar strong scattering in the A_g channel, however, has been observed in HTSC [40].

It was emphasized in Ref. [40] that a multisheeted Fermi surface gives rise to an enhanced scattering contribution of the A_g channel in HTSC, because the mass fluctuations between different sheets of the Fermi surface are not screened. Several authors investigated the band structure and Fermi surface of A_3C_{60} compounds [41–47]. It was found that for the orientationally ordered case the Fermi surface consists of two multiply-connected sheets which are interlinked [42,46]. This complicated structure of the Fermi surface has several possible electron and hole orbits. Unscreened scattering between these orbitals can be responsible for the dominating A_g scattering contribution observed in our spectra. Theoretical calculations implied that the t_{2u} and h_g molecular bands are around 2.4 eV above the Fermi energy [42,48]. In view of the used laser excitation energy (2.4 eV) a resonant interband scattering process in these bands may also be possible which can also lead to an enhanced scattering in the A_g channel.

To detect changes in the electronic scattering intensity the spectra at 4.2 K were normalized to the

spectra that were obtained just above T_c at 35 K . Such normalized spectra are shown in the lower parts of Figs. 1 and 2. At frequencies between 700 and 100 cm^{-1} the relative scattering intensity is nearly constant. At roughly 85 cm^{-1} the intensity shows a sudden decrease clearly reflecting the opening of a gap in the superconducting state.

Fig. 3 shows the normalized $A_g + E_g$ spectra for several temperatures, both below and above T_c . The spectra obtained below T_c show the sharp decrease of the scattering intensity below roughly 85 cm^{-1} . By raising the temperature up to 10 K the onset of the decrease shifts to slightly lower frequencies. For comparison a normalized spectrum recorded at 50 K is shown. It clearly does not show a decrease of the scattering intensity for $\omega \rightarrow 0$, confirming our assignment of the decrease below T_c to a redistribution of the electronic density of states due to the transi-

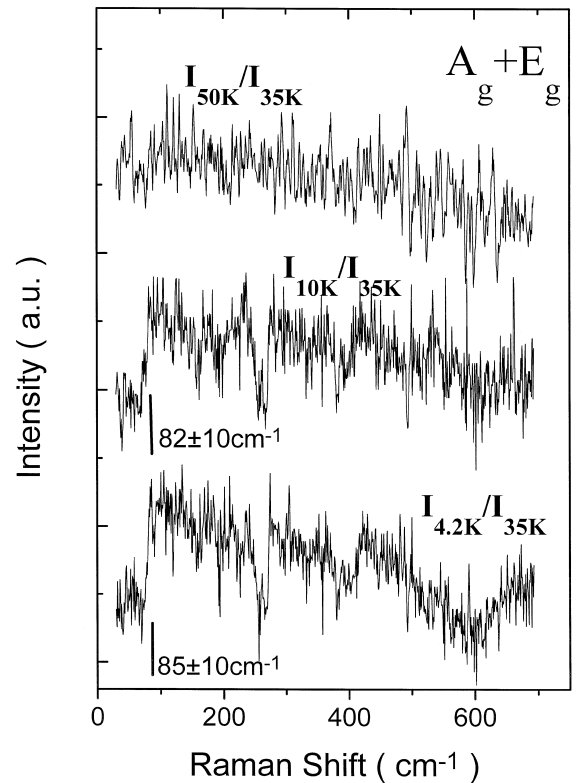


Fig. 3. Normalized Raman spectra of a single crystal of Rb_3C_{60} obtained in $A_g + E_g$ scattering symmetry for the temperatures 50 K , 10 K and 4.2 K (from the top). The spectra have been given an offset for clarity. The gap position for $T < T_c = 31\text{ K}$ is indicated.

tion to the superconducting state. The decrease of the intensity varied from 5 to 50% for the different scattering symmetries at temperatures well below T_c (Fig. 1, lower parts).

The previously discussed Rb–C₆₀ vibration has nearly the same energy as the frequency position of the gap. Since the presence of this mode may influence the above discussed results, we have also calculated the normalized spectra after subtraction of the phonon contribution. The thus normalized spectra (not shown here) again showed the decrease in the scattering intensity due to superconductivity, but with a smeared out edge, and a less sharp decrease in the scattering intensity. Nevertheless, the gap value of $2\Delta = 85 \pm 10 \text{ cm}^{-1}$, extracted using the original spectra, holds within the specified accuracy.

We did not observe any pileup of the scattering intensity at the gap energy typical for an enhancement of the density of states (DOS) at the gap edge in the superconducting state. Such an enhancement with a clear peak was seen in Raman spectra of the A-15 compounds Nb₃Sn and V₃Si, which are typical s-wave superconductors [49]. Our observation is in good agreement with previous photoemission [24], nuclear magnetic resonance (NMR) [25,50], and muon spin relaxation (μ SR) [51] experiments on A₃C₆₀ compounds, which also indicated the absence or weakness of a pileup in the DOS. A possible explanation for a low DOS at the gap edge might originate from the orientational disorder of the A₃C₆₀ compounds. It is known that the DOS at the Fermi level in the normal state is smeared out and slightly reduced due to orientational disorder [43,47], which in turn may lead to a smearing of the pileup peak in the DOS in the superconducting state.

Using $2\Delta = 85 \pm 10 \text{ cm}^{-1}$, we find a gap ratio $2\Delta/k_B T_c = 4.0 \pm 0.5$. This result is independent of the scattering geometry and in agreement with earlier results [21–26,29]. The relatively high value may indicate strong electron–phonon coupling as the origin of superconductivity in fullerenes which is also consistent with our observation that low frequency intermolecular phonons play an important role for the superconductivity.

To discuss the observed gap value one has also to discuss the electronic properties of the A₃C₆₀ compounds. The symmetry of the electronic band at the

Fermi level is the threefold degenerated t_{1u}-band. The possible pair fields in A₃C₆₀ were discussed in Ref. [46]. Besides the symmetric A_g pair field two combinations of an E_g doublet were discussed. By comparing the pairing susceptibility it was found that the symmetric channel should be favored but that the anisotropic channel has only a slightly smaller susceptibility. The real and axial anisotropic pairing field of E_g symmetry results from a simple and a complex combination of the E_g manifold, respectively. The quasiparticle spectral densities show different positions of the logarithmic maxima and also a different behavior for energies smaller than the gap energy. For an axial pairing state the position of the logarithmic singularity in the quasiparticle spectrum was interpreted as the gap value and was found to $2\Delta/k_B T_c = 4.6$ with a non BCS-like temperature dependence.

Our relatively high value for the reduced gap value may support the idea of an anisotropic pairing field. However, the polarization dependent measurements show the same superconducting gap value for different scattering symmetries. The gap is observed as a step-like edge and the intensity ratio below the gap shows no frequency dependence, neither a linear nor a cubic decrease for $\omega \rightarrow 0$. A d-wave order parameter, like in high temperature superconductors, is ruled out by this observation [52].

When one takes a possible influence of disorder into account, an anisotropic gap would be smeared out and becomes more symmetric also leading to a gap value independent on the scattering symmetry. As was discussed previously: especially rotational disorder seems to be an inherent feature in A₃C₆₀ compounds [30]. A possible anisotropy of the superconducting energy gap may therefore be smeared out and may lead to a gap, which is *intrinsically* isotropic, not only for Raman but also for other experiments probing the macroscopic superconducting state. Such an isotropic gap, influenced by disorder, should lead not only to a gap value independent of the scattering geometry but also to in-gap states [53] which are responsible for the only maximum 30% reduction of the scattering ratio observed by us. Therefore, we conclude that the symmetry of the superconducting order parameter should have isotropic s-wave character for Rb₃C₆₀.

4. Conclusion

Rb₃C₆₀ single crystals were investigated by Raman scattering. The intermolecular phonon at 78 cm⁻¹ ($T = 35$ K) shows an upshift of the peak position and a reduction of the width in the superconducting state. These changes strongly indicate that low frequency intermolecular phonon modes give a significant contribution to the electron–phonon coupling in A₃C₆₀ compounds. The observed suppression of the electronic scattering intensity below 85 cm⁻¹ in the superconducting phase has been assigned to the opening of the superconducting gap, leading to a gap value $2\Delta/k_B T_c = 4.0 \pm 0.5$. This relatively high value strongly suggests a strong coupling scenario for the superconductivity in the fullerenes. Because the spectra show the decrease in all measured scattering symmetries at the same position we can fix the order parameter in Rb₃C₆₀ to have isotropic A_g symmetry.

Acknowledgements

We would like to thank B. Beschoten and H. Frank for performing SQUID-measurements. We are grateful for the helpful discussions with P. Fumagalli and D. Einzel. This work was supported by DFG through SFB 341, BMBF Fkz. 13N6586/8 and by Swiss National Science Foundation.

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